Evolution of HCl Concentrations in the Lower Stratosphere from 1991 to 1996 Following the Eruption of Mt. Pinatubo

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In situ measurements of hydrochloric acid (HCl) concentrations in the lower stratosphere from 1991 to 1996 reveal that its abundance relative to that of total inorganic chlorine (Cl_y) has evolved upwards from HCl/Cl_y = 40% in late 1991 to 70% in 1996. The observed fraction is **anticorrelated** with aerosol surface area concentration, which has been diminishing since June 1991 following the volcanic eruption of Mt. Pinatubo. For several years, calculations from **photochemical** models including heterogeneous **chemistry predicted** little change in HCl/Cl_y, and were unable to reproduce these observations. However, calculations incorporating new laboratory results of faster heterogeneous chemistry show that air parcels with high aerosol loading exposed to temperatures of 200-210 K experience enough chlorine activation to drive the HCl/Cl_y fraction below 60%, as observed. This repartitioning of Cl_y increases ozone loss **at all latitudes.**

Introduction

The massive enhancement in aerosol loading of the lower stratosphere following the June 1991 eruption of Mt. Pinatubo *[iMcCormick et al.,* 1995; *Jonsson et al.,* 1996] provided an opportunity to test and develop our understanding of the role of heterogeneous chemistry on sulfate aerosol particles *[Jones et al.,* 1994]. As the dense aerosol volcanic cloud spread into a relatively clean atmosphere, aircraft, balloon, ground-based, and space measurements reported large reductions in concentrations of stratospheric NO_x (NO+ NO_2) relative to those of total reactive nitrogen (NO_y) *[Fahey et al.,* 1993; *Koike et al., 1994; Webster et al.,* 1994a], and in response, a doubling of concentrations of chlorine monoxide (ClO) *[Avallone et al.,* 1993] and chlorine dioxide (OClO) *[Solomon et al.,* 1993]. Heterogeneous hydrolysis of dinitrogen pentoxide (N_2O_5) and chlorine nitrate ($ClONO_2$) to nitric acid (HNO_3) were identified as the reactions responsible for the observed changes in atmospheric composition. Column measurements of HCl before and after the eruption showed no

significant injection of volcanic HCl into the stratosphere [*Mankin et al.,* 1992], and photochemical model calculations incorporating the heterogeneous hydrolysis of N_2O_5 predicted little change (≤ 15 %) in stratospheric HCl amounts despite the large impact on NO_x and ClO_x amounts [*Salawitch et al.,* 1994]. Space-based measurements of either chlorine reservoir HCl or $ClONO_2$ were limited by the dense volcanic cloud to altitudes above the high aerosol loading where heterogeneous chemistry was occurring. *In situ* measurements of $ClONO_2$ have never been made, and in *situ* measurements of HCl below 25 km have only been available (this work) since late 1991, significantly after (he volcanic material had spread.

Since 1992, the stratospheric aerosol loading has decayed considerably; the surface area layer available in 1996 for heterogeneous chemistry has diminished by over an order of magnitude to the low background levels existing before the Pinatubo eruption [*McCormick et al.,* 1995]. Mapping the recovery over the last four years of radical and reservoir abundances to pre-eruption levels offers a rigorous test of models incorporating heterogeneous chemistry, since this period was one of slow reduction in a more homogeneously-distributed aerosol concentration, with more frequent sampling opportunities. During this time, in *situ* aircraft measurements of HCl have been made, and the remote-sensing instruments have been better able to penetrate the volcanic aerosol and sample lower in the stratosphere,

In the lower stratosphere where heterogeneous chemistry has a profound effect on the contribution of the $ClO_x, NO_x,$ and HO_x catalytic cycles to ozone loss (see the review of *Jones et al.,* [1994]), the relative amount of HCl and $ClONO_2$ takes a special importance through chlorine nitrate's role as a temporary reservoir for reactive forms of both chlorine and nitrogen oxides. Unlike HCl, $ClONO_2$ is readily photolyzed to produce Cl or ClO. The relative abundances of HCl and $ClONO_2$ can therefore determine the extent of ozone loss. Although HCl is recognized as the principal reservoir of chlorine in the middle and upper stratosphere, discrepancies exist between models and measurements of HCl both above 24 km where models tend to under-predict HCl abundances [*Michelsen et al.,* 1996], and below 24 km where models over-predict HCl abundances [*Webster et al.,* 1994 b].

Since 1991, JPL's Aircraft Laser Infrared Absorption Spectrometer (ALIAS) instrument *[Webster et al., 1994c] (15)* has flown more than 150 times on the NASA's ER-2 aircraft. HCl mixing ratios first measured by this instrument [*Webster et al.,* 1993] from 15-20 km were about a factor of two lower than model predictions [Salawitch *et al. , 1994].* Results from the 1993 Stratospheric Photochemistry and Aerosols and Dynamics (SPADE) campaign out of Moffett Field, California, illustrated the difficulties in balancing the inorganic chlorine budget using the low HCl measurements. In the absence of *in situ* measurements of $ClONO_2$, simultaneous measurements of ClO, NO_2, and O_3 were used to infer $ClONO_2$ abundances [*Stimpfle et al. , 1994].* With an inferred fraction of $ClONO_2$ / Cl_y of **14%** (ranging from 6 to 28%), the measured ClO amounts implied that if Cl_y

comprised only HCl and $ClONO_2$, I{ Cl/Cl_y should be -86%, compared to the observed value of 40%. The aircraft measurements of 1993 therefore left ≥30% of inorganic chlorine apparently unaccounted for, indicating that the photochemistry involving HCl and $ClONO_2$ was not well understood. An analysis of data recorded in September 1993 during a balloon flight of the MarkIV FTIR spectrometer yielded the proposal that 20-30% of Cl_y may be sequestered as perchloric acid ($HClO_4$) produced from the heterogeneous reaction of ClO and H_2SO_4 on sulfate aerosols [*Jaeglé et* al., 1995]. Two other studies report HCl/Cl_y ratios consistent with both the model predictions of 80% and with the aircraft ALIAS measurements of 1993. These studies include: balloon measurements of ClO at 20 km [*Avallone et al.,* 1993], and a recent analysis of HALOE HCl and CLAES ClONO, measurements from the UARS satellite [*Dessler et al., 1995]* observed between August 1992 and March 1993, both of which reported HCl/Cl_y =60 $\pm$ 20 %. In an intercomparison of 1994 aircraft data with overflights of ATMOS in Nov. 1994, and with an earlier flight of MarkIV in May 1994, the ALIAS data lie midway between the two FTIR data sets for N_2O values ≤210 ppbv, where HCl mixing ratios are ≥ 1 ppbv. ALIAS measurements are about 10% lower than that of ATMOS [*Chang et al.,* 1996], and about 10% higher than those of the MarkIV [G. *Toon,* private communication], for similar ozone abundances.

This paper brings together six years of HCl measurements to show a remarkable consistency in the aircraft data base and its evolution with time from 1991-96. It places earlier HCl measurements in context with those made more recently (1 992-96) during the years of gradual decay of the Mt. Pinatubo aerosol loading of the stratosphere. Particularly intriguing about the time history of the aircraft measurements is the observation of an HCl fraction of total inorganic chlorine (Cl_y), which has increased with time as the Mt. Pinatubo aerosol loading has diminished; values of HCl/Cl_y range from 40% in 1991 /1992 to 70% in 1996, now evolved upward into good agreement with earlier model predictions. We present here model results incorporating new laboratory results of faster heterogeneous chemistry, which show that air masses with high aerosol loading exposed to temperatures typical of the midlatitude lower stratosphere (200-210 K) experience enough chlorine activation to drive the HCl/Cl_y fraction below 60%, as observed. Significant repartitioning of chlorine reservoir species from low-temperature sulfate aerosol chemistry and enhancement in ozone depletion is therefore predicted at all latitudes from even moderate future volcanic activity.

The aircraft instruments

The Aircraft Laser Infrared Absorption Spectrometer (ALIAS) instrument is a 4-channel scanning tunable diode laser spectrometer that uses high-resolution laser absorption in the 3-8 μm wavelength region [*Webster et al.,* 1994c] to directly and simultaneously measure any four of the gases HCl, NO_2, CH_4, CO, and N_2O. Both direct absorption and second - harmonic detection techniques are used to measure the fractional absorption from individual or groups of rovibrational lines for each gas, with line-center absorption typically a few percent for the tracers N_2O, CH_4, and CO, and less than 0.05% for HCl and NO_2. The instrument samples the atmosphere using a fast flow system with a flow rate of 16 liters/see

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at 65 mbar driven by inlet ram pressure and by aerodynamic vacuum at the exhaust. The flow system is in two parts, a heated inlet with wall temperatures of 60-70°C, and a multipass optical (Herriott) cell. All interior surfaces are coated with a halocarbon wax from a chloroform solution to minimize wall loss. Extensive calibration and testing of the inlet and sampling system, including post-flight ion-analysis of the inlet residue, has revealed no systematic instrument or sampling error that could result in HCl loss of greater than 10%. The fidelity of the measurement of HCl in the mult i -pass cell is checked by simultaneous recording of strong CH_4 lines close to the HCl absorption line. The precision of the data can vary from flight to flight, but is typically a constant value of about 0.05 ppbv. The accuracy of the measurement is about 5-7%, producing total measurement uncertainties of about 10-15% for HCl.

The aerosol number, surface area, and volume concentrations reported here were determined from three particle size spectrometers flown simultaneously as part of the ER-2 aircraft payload, with overall uncertainties of 35% estimated from intercomparison. The condensation nucleus counter (CNC) measured particle concentrations larger than 0.008 μm in diameter [Wilson et al., 1983], with an accuracy of a few percent. The focused cavity aerosol spectrometer (FCAS) instrument measured size distributions from 0.06 to 2 μm diameter range [Wilson et al., 1992], producing a particle size spectrum every 10 seconds. The forward scattering spectrometer probe (FSSP-300) detected particles between (1.4 and 20 μm diameter [Baumgardner et al., 1992], and flew on the ER-2 during 1991/2 and 1993. We used measurements from FSSP for AASE-II, from FCAS for ASHOE/MAESA and STRAT, and from all three spectrometers for SPADE.

For most of the flight data presented here, the tracer N_2O was measured directly by the ALIAS instrument. However, for a few flights in which ALIAS data were unavailable or of poor quality, N_2O measurements from the Airborne Tunable Laser Absorption Spectrometer (ATLAS) instrument [Podolske and Loewenstein, 1993] were used. ClO was measured using resonance fluorescence detection of Cl atoms at 118.9 nm, generated by chemical conversion of ambient ClO to Cl by addition of NO [Stimpfle et al., 1994]. O_3 was measured using UV absorption [Proffitt et al., 1983].

The aircraft measurements of HCl

Figure 1 shows plots of HCl vs. N_2O recorded by the ALIAS instrument as part of the payload of the ER-2 aircraft during four major missions: the 1991/2 Airborne Arctic Stratospheric Expedition (AASE-II), the 1993 SPADE experiment, the 1994 Airborne Southern Hemisphere Ozone Expedition/Measurements of the Atmospheric Effects of Stratospheric Aircraft (ASHOE/MAESA), and the 1996 Stratospheric Tracers of Atmospheric Transport (STRAT) mission. These data are principally from latitudes between 20° and 70° N and have been restricted to pressures less than 67 mbar and ClO amounts less than 150 pptv to remove data from air masses that have undergone severe heterogeneous low-temperature processing. Also plotted are the calculated values of Cl_y

expected from the observed N_2O values and a polynomial least-squares fit to the data.

The 1991 /2 AASE-II data collected from a series of flights from 4 Ott. 1991 through 22 March 1992 fail mainly within a single correlation group except for the striking anomalies from the two earliest flights of 4 Oct. (blue triangles) and 6 Oct. (black diamonds) 1991. These latter two flights covered the latitude range 37-85 "N and were sufficiently close in time to the June 1991 eruption of Mt. Pinatubo to sample regions of rapidly-changing aerosol load ing [*Jonsson et al., 1992*]. The data from these two early flights appear divided into two populations of low and high HCl values, whose variation with aerosol surface area is described later. The 1993 SPADE HCl values are generally more tightly correlated with measured N_2O, except the flights of 11 May (orange triangles) and 1 May (green circles) 1993, which are not included in the least-squares correlation fit. From tracer correlations, these flights have been identified as sampling air more typical of midlatitudes than of polar origin [*Michelsen et al., 1997a*] (see next section).
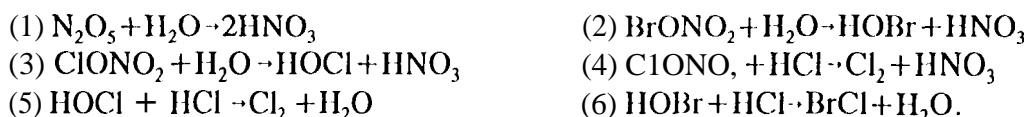
The least-squares fits of Fig. 1 from each mission are plotted in Fig. '2A, where an evolution with time of the HCl/Cl$_y$ ratio is apparent. The data from 1991/2 (AASE-II), 1993 (SPADE), 1994 (ASHOE/MAESA), and 1996 (STRAT) show HCl/Cl$_y$ fractions of typically 40%, 50%, 55-60%, and 75%, a trend that is maintained with latitude within the range 40-60 "N, as shown in Fig. 2B, where data from all missions are included.

Chlorine activation on sulfate aerosols

The chemistry responsible for the formation of the ozone hole is initiated by the heterogeneous conversion of reservoir species such as HCl and ClONO, to reactive radicals (such as Cl and ClO), a process known to occur on the surfaces of polar stratospheric cloud (PSC) pat titles and supercooled liquid sulfate aerosols, as described in the review by *Fahey et al.* [1995]. This heterogeneous loss of HCl is associated with low temperatures, i.e., less than 195 K, and is not expected to be significant at higher temperatures.

In a recent study of ATMOS, SAGE 11, and UARS data from the northern hemisphere polar vortex, however, *Michelsen et al.* [1997b] concluded that reactions mediated by liquid sulfate aerosols (60% wt.) could have a greater effect than previously believed on the midlatitude partitioning of Cl$_y$ and NO$_y$ species, and on global ozone loss throughout the lower stratosphere. These reactions were found to repartition Cl$_y$ and NO$_y$ at temperatures warmer than 197 K, which are more typical of those existing outside the polar vortex. In a second study, these authors studied correlations of CH_4, N_2O, NO_y, H_2O, and aerosol abundances from ATMOS, SAGE, and ER-2 data sets to discriminate between vortex, midlatitude, and tropical air masses. From this framework, it was identified [*Michelsen et al., 1997a*] that much of the air sampled during SPADE had the tracer signatures of polar air, characterized by low CH_4, low NO_y, low O_3, high aerosol surface area, low HCl, and low H_2O amounts. Aircraft data from other years were not considered.

We have tailored the heterogeneous model results of *Michelsen et al.* [1997a,b] to estimate the sensitivity of the ratio HCl/Cl_y to aerosol surface area concentration and temperature for comparison with the aircraft data, to assess whether heterogeneous sulfate chemistry can quantitatively reproduce the observations of a five-year data base. In Fig. 4A the flight-average HCl/Cl_y ratios vs. aerosol surface concentration for all flights studied are compared with those calculated by a model assuming photochemical steady state and incorporating the full set of heterogeneous reactions:

$$(1)\ N_2O_5 + H_2O \rightarrow 2HNO_3 \qquad\qquad (2)\ BrONO_2 + H_2O \rightarrow HOBr + HNO_3$$
$$(3)\ ClONO_2 + H_2O \rightarrow HOCl + HNO_3 \qquad (4)\ ClONO_2 + HCl \rightarrow Cl_2 + HNO_3$$
$$(5)\ HOCl + HCl \rightarrow Cl_2 + H_2O \qquad\qquad (6)\ HOBr + HCl \rightarrow BrCl + H_2O.$$

At temperatures below about 206 K, these reactions proceed rapidly enough on liquid sulfuric acid (60 wt%) aerosol particles to provide a significant channel for Cl production at the expense of HCl, leading to enhanced $ClONO_2$ production from the gas-phase reaction of NO_2 and ClO. In this way the partitioning of Cl_y between HCl and $ClONO_2$ is shifted from HCl dominance to that of $ClONO_2$. The importance of including heterogeneous bromine chemistry has been emphasized by the recent studies of *Lary et al.* [1996] and *Tie and Brasseur [1996]*, whose studies suggested that significant reduction in HCl/Cl_y could be achieved from low temperature heterogeneous bromine chemistry alone. Within the 16-19 km region from which the ALIAS data predominantly originates, our model calculations show that reactions (4) and (5) account for 40-50% each of the repartitioning, with reactions (1), (2), (3), and (6) making little ($\leq$ 15 %) contribution.

Since HCl/Cl_y has a significant dependence on O_3 abundance, we first restrict data to points lying in the range $1500 \leq O_3 \leq 2500$ ppbv (with the additional restrictions of $N_2O \leq 260$ ppbv, pressure ≤ 67 mbar, ClO $\leq$ 150 pptv, and sza $\leq 82°$). A plot of HCl/Cl_y against aerosol surface area concentration shows that with few exceptions (4 and 6 Oct. 1991; 1 and 11 May 1993; included in Fig. 4 and discussed later), flights from 1991-6 appear to demonstrate a smooth decay in HCl/Cl_y with increasing surface area, as shown in Fig. 3. The lower panel is a fit to the flight-average points using an exponential decay function.

The flight averages of Fig. 3 are included with those of 4 and 6 Oct. 1991, and of 1 and 11 May, 1993, for comparison with model calculations run at several temperatures initialized with values of NO_y, CH_4, O_3, H_2O, and N_2O measured during the flight of 2 Nov. 1994. For high surface area concentrations, the observed decay in HCl/Cl_y is generally well-represented in Fig. 4 by the model calculations for a temperature of about 207 K. There is a tendency, however, for the observed decay to be steeper at lower surface areas, and flatter at larger surface areas. A more thorough analysis based on conditions measured for each flight is again more consistent with the measurements than the results of previous modeling studies, but still shows disagreement with measured values when photochemical steady-state is assumed for the instantaneous temperatures measured during

the flight. For the high surface area flight of 17 February 1992, for example, in which temperatures of 210-225 K were encountered with a mean HCl/Cl_y value close to 0.4, flight-tailored model calculations produce HCl/Cl_y values of 0.2, 0.49, and 0.67 for temperatures of 205, 207, and 221 K, respectively. The model results are sensitive to the duration of low temperatures recently encountered, and back-trajectory calculations of the temperatures experienced by the sampled air masses are needed for all of the flights for better comparison with the model results. During the AASE-II, ASHOE/MAESA, and STRAT missions, flight temperatures were rarely lower than 210-215 K, but during the SPADE mission flight temperatures in the range 203-208 K were often recorded; this range therefore represents an upper value for the minimum temperatures experienced over the last few days. The flights of 1 and 11 May 1993 were recorded at the higher temperatures of 215-220 K, and 220 K, respectively, and the flight average HCl/Cl_y ratios are seen in Fig. 4 to be higher than the 1992-96 fit. Tracer correlations indicate that these flights should be in photochemical steady-state for midlatitude conditions, consistent with the model results.

Because the combination of high surface area and moderately cold temperature is necessary to repartition HCl, an altitude dependence to HCl/Cl_y is expected. Above ER-2 altitudes, temperatures are generally warmer. The pressure-dependent HCl vs. N_2O relationship shown by several data sets [*Webster et al.,* 1994b] may reflect the ineffectiveness of aerosol chemistry at the altitudes above the ER-2 where higher temperatures are found, despite the enhanced aerosol loading.

Also plotted in Fig. 4 are the flight-average data for the early flights of 4 and 6 Oct. 1991, which have particularly low HCl/Cl_y ratios for surface area concentrations only 2-5 times background levels. Although the model calculations suggest that these data may be from air masses that had earlier experienced temperatures of 203 K or less, temperatures this low are not generated from back trajectory calculations five days before the flights. Looking back at Fig. 1A, the striking fractionation of the HCl vs. N_2O correlation plot seen for October 1991 appears to represent a case intermediate between the SPADE (high aerosol) and STRAT (low aerosol) data. The initial volcanic material spreading out from the lower latudes is known to have different chemical composition than the aerosol characteristic of the later decaying period, and it may be that the heterogeneous rates are even faster on the smaller, younger sulfate aerosol matter.

The observed dependence of ClO/Cl_y on aerosol surface concentration is also compared with model predictions in Fig. 4. These data have been selected to cover a narrow range of solar zenith angles (62-82 0), and have been normalized to O_3 amount with a small correction term generated from the observed dependence of ClO/Cl_y on measured ozone. The SPADE C1O data of May 1993 [*Stimpfle et al.,* 1994] are significantly lower than the 1991/2 C1O data [*Toohey et* al., 1993] for similar particle surface area concentrations of around 2-6 $\mu m^2/cm^3$, due to higher NO_x values. These lower C1O data of SPADE were used [*Stimpfle et al.,* 1994] to infer (low) $ClONO_2/Cl_y$ ratios, which were discrepant with

the direct HCl/Cl_y measurements of ALIAS. When dependence on NO_x is taken into account, the consistency between the model calculations and the measured ClO/Cl_y is very good. However, the plots of Fig. 4 illustrate that a discrepancy between ClO/Cl_y and HCl/Cl_y still remains, in that the temperatures needed to match the HCl/Cl_y observations are somewhat lower than those needed for ClO/Cl_y. Nevertheless, the model results do show that low HCl/Cl_y values of 40% can be expected in a high aerosol environment at only moderately low (≤ 207 K) temperatures. Furthermore, these results are consistent with the results of a companion paper [*Dessler et* al., 1997], which report HALOE satellite observations of a 26% increase in HCl/Cl_y from 1992 to 1996.

The observed dependence of lower stratospheric HCl concentration on surface area concentration over the five-year period following the volcanic eruption of Mt. Pinatubo demonstrates that aerosol chemistry at temperatures ≥ 200 K has a more pronounced effect on Cl_y partitioning than previously believed. Lower HCl/Cl_y ratios are associated with increased reactive chlorine, products of enhanced heterogeneous chemistry on sulfate aerosol which is responsible [*Michelsen et al., 1997*] for the underestimation by atmospheric models [*Solomon et* al., 1996] of observed ozone loss in volcanic aerosol conditions.

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FIGURE CAPTIONS

Figure 1. HCl vs. N_2O from 1991 through 1996, compared with expected total inorganic chlorine (Cl_y) mixing ratios calculated from the N_2O values [*Woodbridge et al.,* 1995]. The dashed lines are polynomial fits to the data, where the flights of Ott. 4 and 61991, and those of May 1 and 11 1993 are not included.

Figure 2. A. Superposition of the polynomial fits of Fig. 1 to the ALIAS HCl vs. N_2O mixing ratios divided by Cl_y, showing the apparent time evolution. B. Measured HCl/Cl_y vs latitude over the range 40-60 "N for data constrained by: pressures 67 mbar, $N_2O \le 260$ ppbv, $ClO \le 150$ pptv, and $1500 \le O_3 \le 2500$ ppbv. The solid lines are the average values over the given latitude range to illustrate the apparent evolution with time of HCl/Cl_y over this latitude range.

Figure *3.* Measured HCl/Cl_y *vs* aerosol surface area concentration for several flights from December 81992 through July 2.21996. All data are constrained by: pressures 67 mbar, $N_2O \le 260$ ppbv, and $ClO \le 150$ pptv, and $1500 < O_3 \le 2500$ ppbv. The lower panel shows the flight-average values with one-sigma standard deviations from the mean, and an exponential least-squares fit to the flight-average points.

Figure 4. Comparison between theory and measurements. Flight-average values of HCl/Cl_y and ClO/Cl_y *vs* aerosol surface area are constrained by pressure< 67 mbar, $N_2O \le 260$ ppbv, $ClO \le 150$ pptv, and $1500 \le O_3 \le 2500$ ppbv. In addition to the flights of Fig. 3, flights of Oct. 4 and 6, 1991, and May 1 and 11, 1993 are included. Calculated values at 18 km are plotted for temperatures of 2.01, 204, and 230 K.
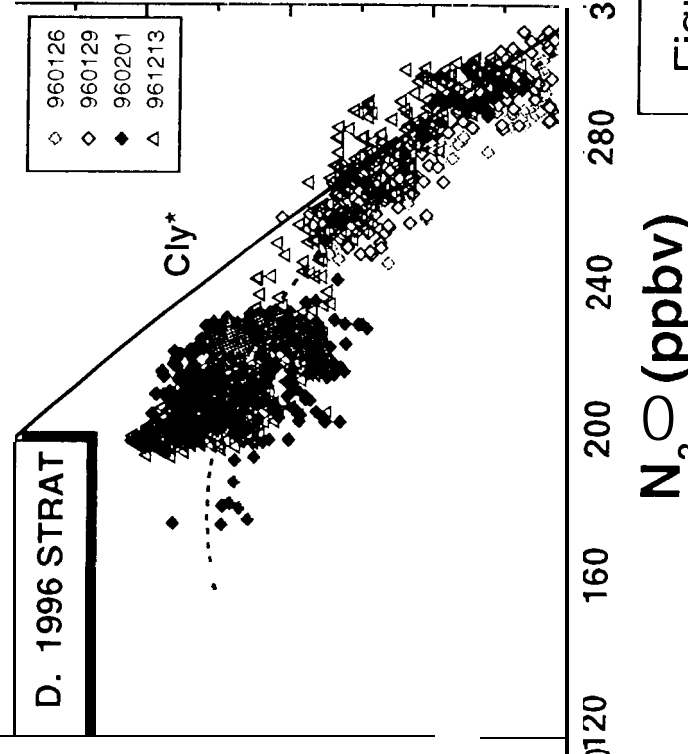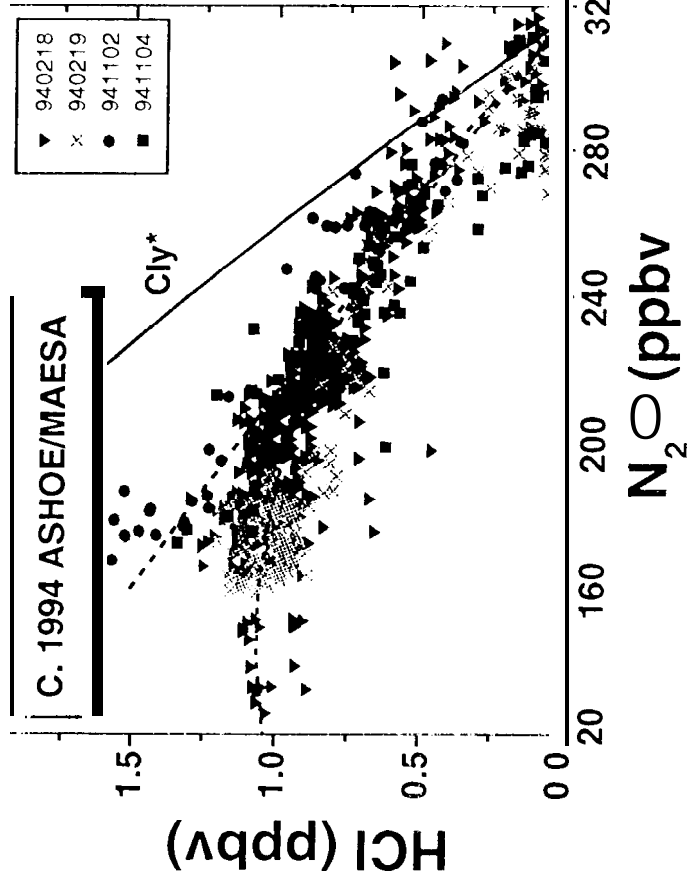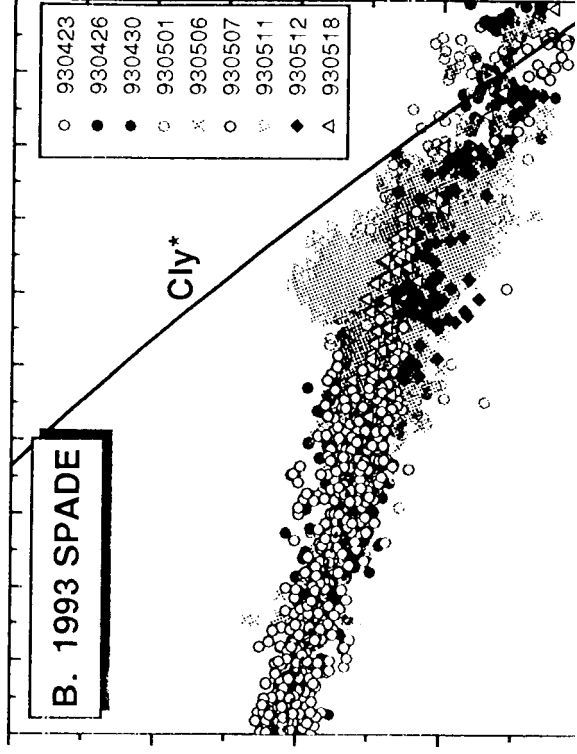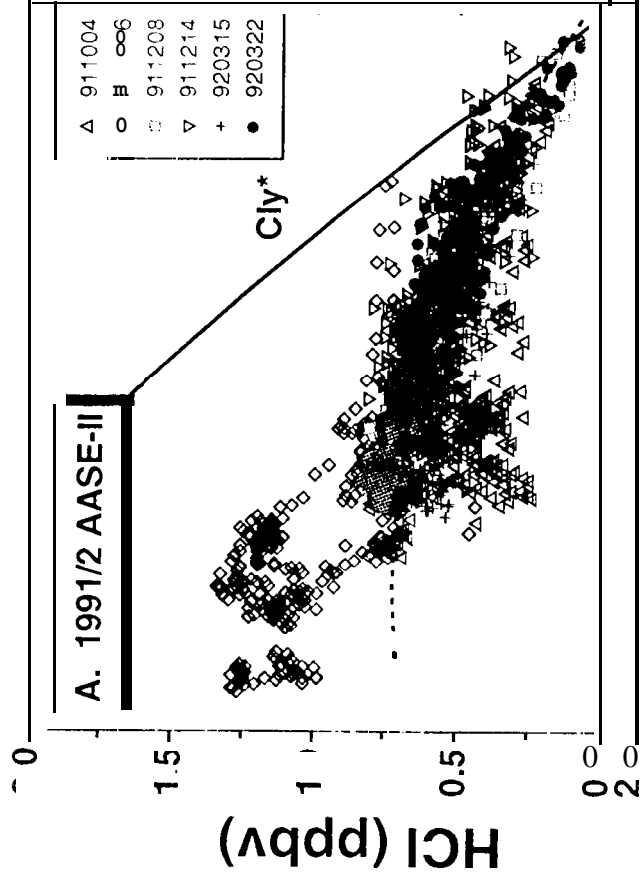
Figure 1

Figure 2

Figure 3

Figure 4

Upper panel — y-axis: HCl/Cl$_y$; x-axis: Aerosol surface area (μm^2/cm^3)

Legend: △ 911004　◇ 911006　○ 930501　▽ 930511

Curves labeled: 215 K, 204 K, 201 K

Lower panel — y-axis: ClO/Cl$_y$; x-axis: Aerosol surface area (μm^2/cm^3)

Curves labeled: 201 K, 204 K, 215 K